



**INFLUENCE OF MEDIA SIZE AND FLOW RATE ON THE TRANSPORT OF
SILVER NANOPARTICLES IN SATURATED POROUS MEDIA:
LABORATORY EXPERIMENTS AND MODELING**

THESIS

Travis J. Meidinger, Major, USAF

AFIT-ENV-13-M-15

**DEPARTMENT OF THE AIR FORCE
AIR UNIVERSITY**

AIR FORCE INSTITUTE OF TECHNOLOGY

Wright-Patterson Air Force Base, Ohio

DISTRIBUTION STATEMENT A
APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.

The views expressed in this thesis are those of the author and do not reflect the official policy or position of the United States Air Force, Department of Defense, or the United States Government. This material is declared a work of the United States Government and is not subject to copyright protection in the United States.

INFLUENCE OF MEDIA SIZE AND FLOW RATE ON THE TRANSPORT OF
SILVER NANOPARTICLES IN SATURATED POROUS MEDIA: LABORATORY
EXPERIMENTS AND MODELING

THESIS

Presented to the Faculty

Department of Systems and Engineering Management

Graduate School of Engineering and Management

Air Force Institute of Technology

Air University

Air Education and Training Command

In Partial Fulfillment of the Requirements for the
Degree of Master of Science in Environmental Engineering

Travis J. Meidinger, BS

Major, USAF

March 2013

DISTRIBUTION STATEMENT A
APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.

INFLUENCE OF MEDIA SIZE AND FLOW RATE ON THE TRANSPORT OF
SILVER NANOPARTICLES IN SATURATED POROUS MEDIA: LABORATORY
EXPERIMENTS AND MODELING

Travis J. Meidinger, BS
Major, USAF

Approved:

LEEANN RACZ, Maj, USAF, BSC, PhD, PE (Chairman)

Date

MARK GOLTZ, PhD (Member)

Date

SUSHIL KANEL, PhD (Member)

Date

CHRISTOPHER IMPELLITTERI, PhD (Member)
USEPA, Cincinnati, OH

Date

Abstract

Silver nanoparticles (AgNPs) are widely produced and used. Because of their potential toxicity and the possibility of their release into the environment, it is important to understand the factors involved in their transport; particularly how they may move in groundwater, which is a potential pathway to human and environmental receptors. By passing a solution of 15 mg/L AgNPs with an average size of 17 nm through sand-filled glass columns, this study looks at the physical effects of flow rate and media size on transport. Three different sand sizes (< 0.074 , 0.21-0.297, and 0.4-2.0mm) were used, as well as two different flow rates (1 and 4 mL min⁻¹). Results showed that flow rate had little effect on the transport of AgNPs. As had been found in previous studies, transport through fine sand (< 0.074 mm) was inhibited, and no AgNPs were observed in the column effluent. In contrast to other studies and conventional filtration theory, however, it was observed that more AgNPs were captured in the coarse sand (0.4-2.0 mm) than the medium sand (0.21-0.297 mm). This deviation from conventional filtration theory was attributed to the more heterogeneous size distribution of the coarse sand compared to the medium sand.

Acknowledgment

The support of the Air Force Medical Support Agency's Research and Innovation Division (AFMSA/SG51), Department of Defense Funding Document No. F1ATD42054G001, is gratefully acknowledged.

Table of Contents

	Page
Abstract	iv
Acknowledgment.....	v
Table of Contents	vi
List of Figures	vii
List of Tables	viii
 I. Introduction	 10
Problem Statement	122
Research Objectives	133
Preview.....	133
 II. Scholarly Article	 144
Abstract	144
Introduction	155
Materials and Methods	177
<i>Materials</i>	177
<i>Sand Preperation</i>	188
<i>Column Experiments</i>	188
<i>Analysis</i>	20
<i>Mass Balance Experiment</i>	22
Results and Discussion.....	255
<i>Characterization of AgNPs</i>	25
<i>Characterization of Sand</i>	25
<i>Transport of AgNPs</i>	256
<i>Model Simulations of AgNP Transport</i>	289
Significance.....	30
Acknowledgements	30
Disclaimer	31
Bibliography.....	311
 III. Conclusion	 32
Summary of Findings	322
Recommendations for Future Research	322

	Page
Bibliography	40

List of Figures

	Page
Figure 1: a) HRTEM images of AgNPs and b) size histograms prepared based on analysis of the HRTEM images of > 500 AgNPs	34
Figure 2: Coarse sand BTC for a) tracer and model simulation for 1 and 4 mL min ⁻¹ b) Coarse sand 1 mL min ⁻¹ and model simulation for AgNP c) Coarse sand 4 mL min ⁻¹ and model simulation for AgNP.....	35
Figure 3: BTC for a) Medium sand column tracer and model simulation for 1 and 4 mL min ⁻¹ b) Medium sand column and 1 mL min ⁻¹ and model simulation c) Medium sand column and 4 mL min ⁻¹ and model simulations.....	36
Figure 4: BTC for coarse and medium sand column and 1 mL min ⁻¹ with the corresponding model for each.....	37
Figure 5: BTC for coarse sand column and 4 mL min ⁻¹ plotted with ICP and UV-vis data	37
Figure 6: BTC for coarse sand column and 4 mL min ⁻¹ taken at time zero and coarse sand column and 4 mL min ⁻¹ taken at time five months measured on UV-Vis.....	38
Figure 7: BTC for coarse sand column and 4 mL min ⁻¹ measured on the ICP-OES.....	38

List of Tables

	Page
Table 1: Breakthrough curve moments for AgNP at different flow rates and sand sizes.	33
Table 2: Breakthrough curve moment ratios when compared to its respective tracer for AgNP at different flow rates and sand sizes.....	33
Table 3: Model parameter values at different flow rates and sand size.....	33

INFLUENCE OF MEDIA SIZE AND FLOW RATE ON THE TRANSPORT OF SILVER NANOPARTICLES IN SATURATED POROUS MEDIA: LABORATORY EXPERIMENTS AND MODELING

I. Introduction

Research on silver nanoparticles (AgNPs) has increased recently because of their extensive use in consumer products (Benn et al. 2010; Impellitteri et al. 2009), medical and pharmaceutical supplies (Faunce and Watal 2010), environmental applications and electronics (Kim et al. 2007; Tolaymat et al. 2010; Wijnhoven et al. 2009). Some of these studies have shown that AgNPs may have toxic effects on the environment, aquatic organisms and human health (Kim et al. 2008; Wijnhoven et al. 2009; Schrand et al. 2010; Kennedy et al. 2010; Shaw and Handy 2011). Because of their toxicity and ubiquity, it is necessary to better understand the fate and transport of AgNPs in the environment. In particular, understanding the fate and transport of AgNPs in groundwater is necessary, as groundwater is an important pathway of AgNPs to human and environmental receptors (Flory et al., 2013).

Filtration theory presented by Yao et al. (1971) posits that there are three main mechanisms that affect the capture of particles in porous media. The three mechanisms are advection (interception), diffusion and gravity (sedimentation). Yao et al. (1971) state that removal of particles in the size range of AgNPs (<100 nm) would be controlled by diffusion.

Because diffusion is the primary mechanism controlling AgNP transport, as the velocity of the fluid increases the percentage of particles or mass that the filter captures

decreases. In addition, as the media size decreases the efficiency of the filter should increase. This means that for AgNP transport through porous media, more particles will be collected as the media diameter gets smaller.

Li et al. (2008) conducted studies on the effect that two flow rates had on the transport of Fullerene nanoparticles with four fractions of Ottawa sand. In accordance with filtration theory, they found that as the media size or flow rate decreased, a higher fraction of mass was retained in the media.

Multi-walled carbon nanotube (MWCNT) transport was studied by Mattison et al. (2011). They found with different flow rates and sand sizes that MWCNT retardation increased with decreasing collector size, which is in accord with colloid filtration theory. In their study two pulses of MWCNTs were injected into the column. They found that deposition rate decreases as their experiments progressed and this could not be predicted with traditional colloid filtration theory. They indicated that chemical and physical heterogeneity, both of which would be expected in subsurface environments, could affect transport and are important topics for future research.

Some studies have been conducted to determine the effect of media heterogeneity on the transport of various bacteria, viruses and colloids. Silliman et al. (2001) found that some strains of bacteria traveled through a homogenous porous media better than a more heterogeneous one. One important finding was that as media heterogeneity increased, the percentage of mass leaving their column decreased. In their study they quantified their heterogeneity by the hydraulic conductivity and range of grain sizes. Also Redman et al. (2001) evaluated the impact of media heterogeneity on pathogen filtration. They found

that heterogeneity at the scale of the pathogen or the collector (microscale) leads to a slow decay of concentration versus the fast exponential decay predicted by standard filtration theory. They also found that heterogeneity at the filter scale (macroscale) can have large effects on the transport of viruses. This macroscale heterogeneity describes the difference in size of grains in the filter versus the microscale which describes how smooth or rough individual particles are within the media.

Previous work that has investigated the effect of flow rate and media size on engineered nanoparticles (ENPs) transport has used various ENP types. This study focuses on how flow rate and media grain size affects the transport of AgNPs, which due to their toxicity and ubiquity are of particular importance. Specifically, this study will focus on what physical processes are relevant to the transport of AgNPs in porous media and what model governing equations and parameter values are appropriate to describe AgNP fate and transport in porous media under varying hydrogeological (flow rate and media size) conditions.

Problem Statement

While several studies have looked at ENP transport in porous media at different media grain sizes and flow rates none, to the authors' knowledge, have conducted a focused investigation on how these two factors in particular affect transport of AgNPs. This study focuses on how flow rate and media grain size affects the transport of AgNPs.

Research Objectives

The objective of this study was to further understand how AgNPs are transported in groundwater. Specifically, the following questions are answered:

1. What physical processes are relevant to transport of AgNPs in sand?
2. What model governing equations and parameter values are appropriate to describe AgNP fate and transport in porous media under varying hydrogeological (flow rate and media size) conditions?

Preview

This thesis is written using the scholarly article format. Chapter II contains a manuscript intended for submission to a peer-reviewed journal. The manuscript includes an abstract, along with introduction, materials and methods, and results and discussion sections. Chapter III provides a summary of the primary findings discussed in the article, as well as related topics for future study.

II. Scholarly Article

Influence of media size and flow rate on the transport of silver nanoparticles in saturated porous media: Laboratory experiments and modeling

Travis Meidinger, Sushil R. Kanel, LeeAnn Racz, Chelsea Marcum, Mark N. Goltz

Abstract

Silver nanoparticles (AgNPs) are widely produced and used. Because of their potential toxicity and the possibility of their release into the environment, it is important to understand the factors involved in their transport; particularly how they may move in groundwater, which is a potential pathway to human and environmental receptors. By passing a solution of 15 mg/L AgNPs with an average size of 17 nm through sand-filled glass columns, this study looks at the physical effects of flow rate and media size on transport. Three different sand sizes (< 0.074 , 0.21-0.297, and 0.4-2.0mm) were used, as well as two different flow rates (1 and 4 mL min⁻¹). Results showed that flow rate had little effect on the transport of AgNPs. As had been found in previous studies, transport through fine sand (< 0.074 mm) was inhibited, and no AgNPs were observed in the column effluent. In contrast to other studies and conventional filtration theory, however, it was observed that more AgNPs were captured in the coarse sand (0.4-2.0 mm) than the medium sand (0.21-0.297 mm). This deviation from conventional filtration theory was attributed to the more heterogeneous size distribution of the coarse sand compared to the medium sand.

Introduction

Silver nanoparticles (AgNPs) have been studied much as of late because of their extensive use in consumer products (Benn et al. 2010; Impellitteri et al. 2009), medical and pharmaceutical supplies (Faunce and Watal 2010), environmental applications and electronics (Kim et al. 2007; Tolaymat et al. 2010; Wijnhoven et al. 2009). Some of these studies have shown that AgNPs have potentially toxic effects for the environment, fish and humans (Kim et al. 2008; Wijnhoven et al. 2009; Schrand et al. 2010; Kennedy et al. 2010; Shaw and Handy 2011). Because of their toxicity and ubiquity, it is necessary to better understand the fate and transport of AgNPs in the environment. In particular, understanding the fate and transport of AgNPs in groundwater is necessary, as groundwater is an important pathway of AgNPs to human and environmental receptors (Flory et al., 2013).

Filtration theory presented by Yao et al. (1971) posits that there are three main mechanisms that affect the capture of particles in porous media. The three mechanisms are advection (interception), diffusion and gravity (sedimentation). Yao et al. (1971) state that removal of particles in the size range of AgNPs (<100 nm) would be controlled by diffusion.

Because diffusion is the primary mechanism controlling AgNP transport, as the velocity of the fluid increases the percentage of particles or mass that the filter captures decreases. In addition, as the media size decreases the efficiency of the filter should increase. This means that for AgNP transport through porous media, more particles will be collected as the media diameter gets smaller.

Li et al. (2008) conducted studies on the effect that two flow rates had on the transport of Fullerene nanoparticles with four fractions of Ottawa sand. In accordance with filtration theory, they found that as the media size or flow rate decreased, a higher fraction of mass was retained in the media.

Multi-walled carbon nanotube (MWCNT) transport was studied by Mattison et al. (2011). They found with different flow rates and sand sizes that MWCNT retardation increased with decreasing collector size, which is in accord with colloid filtration theory. In their study two pulses of MWCNTs were injected into the column. They found that deposition rate decreases as their experiments progressed and this could not be predicted with traditional colloid filtration theory. They indicated that chemical and physical heterogeneity, both of which would be expected in subsurface environments, could affect transport and are important topics for future research.

Some studies have been conducted to determine the effect of media heterogeneity on the transport of various bacteria, viruses and colloids. Silliman et al. (2001) found that some strains of bacteria traveled through a homogenous porous media better than a more heterogeneous one. One important finding was that as media heterogeneity increased, the percentage of mass leaving their column decreased. In their study they quantified their heterogeneity by the hydraulic conductivity and range of grain sizes. Also Redman et al. (2001) evaluated the impact of media heterogeneity on pathogen filtration. They found that heterogeneity at the scale of the pathogen or the collector (microscale) leads to a slow decay of concentration versus exponential decay predicted by standard filtration theory. They also found that heterogeneity at the filter scale (macroscale) can have large

effects on the transport of viruses. This macroscale heterogeneity describes the difference in size of grains in the filter versus the microscale which describes how smooth or rough an individual particles are within the media.

Previous work that has investigated the effect of flow rate and media size on engineered nanoparticles (ENPs) transport has used various ENP types. This study focuses on how flow rate and media grain size affects the transport of AgNPs, which due to their toxicity and ubiquity are of particular importance. Specifically, this study will focus on what physical processes are relevant to the transport of AgNPs in porous media and what model governing equations and parameter values are appropriate to describe AgNPs fate and transport in porous media under varying hydrogeological (flow rate and media size) conditions.

Materials and Methods

Materials

Two types of sand were purchased for these experiments. The first was 50-70 mesh sand (0.297-0.21 mm) from Sigma-Aldrich (St. Louis, MO). The second sand was Quikrete 50 lb. Commercial Grade Medium Sand (Atlanta, GA) with an advertised size range of 20-50 mesh (0.841-0.297 mm). A 1000 mg L⁻¹ suspension of PVP doped AgNPs (hereafter referred to as AgNPs) (99.99% pure) was purchased from US Research Nanomaterials, Inc. (Houston, TX). ACS reagent grade HNO₃ was purchased from Sigma-Aldrich (St. Louis, MO). The reagents were used as received.

Sand Preparation

The Quikrete sand was sieved to produce a 10-40 mesh fraction (0.4-2 mm) and a >200 mesh (<0.074 mm) fraction. The two size fractions were stored in individual sealed glass containers. Each size fraction was then acid washed. The sand was put in a Buechner funnel with Whatman No 42 filter paper on top of the sand. The sand was then rinsed with water and the water was vacuumed off. The funnel was then filled with 15.9N HNO₃ and allowed to sit for 5 min. The sand was then rinsed with aliquots of reverse osmosis (RO) purified water until it reached a pH of 7.0. It was then dried in an oven at 300° C for two hours. Once dry, the sands were placed in clean sealed glass containers. The Sigma-Aldrich 50-70 mesh sand was used as it came from the supplier, without additional preparation.

Column Experiments

A glass column (2.5 cm inner diameter × 5 cm length) was packed with 42g, 45g or 44g of 10-40 mesh (0.4-2 mm), 50-70 mesh (0.21-0.297 mm), or >200 mesh (<0.074 mm) sand respectively (referred to as coarse, medium and fine sand throughout this paper), and 0.1 g of glass wool was added to each end of the column to keep the media in the column. The column was packed wet for each experiment to ensure no cross contamination between experiments. Deionized (DI) water was passed through the column for approximately 30 minutes to ensure there were no leaks or air bubbles in the column or tubing. The flow rate was set on a peristaltic pump (0–100 rpm, MasterFlex) to 1 or 4 mL min⁻¹ depending on the experiment being run. The flow rate was measured by measuring the volume of solution that was captured by the fraction collector as a

function of time for each experiment. Once the desired flow rate was reached, tracer solution (60 mL of 3 mM aqueous KCl solution) and/or AgNP (60 mL of 15 mgL⁻¹ AgNP suspension) was passed through the column. The solutions were added for 15 minutes at 4 mL min⁻¹ or 60 min at 1 mL min⁻¹. After the allotted time, DI water was then passed through the column for an additional 30 or 120 minutes for the 4 and 1 mL min⁻¹ runs, respectively. The flow rate was monitored throughout the experiment and adjusted if needed. The effluent was passed through an open cell in an Ultraviolet–visible (UV-vis) spectrophotometer (UV-Cary 60, Agilent). Readings were taken on the UV-vis every 30 seconds for the 4 mL min⁻¹ experiment and every 2 minutes for the 1 mL min⁻¹ experiment. The UV-vis was zeroed prior to each run with DI water. In addition a calibration curve was developed by using AgNPs at a concentration of 50, 25, and 12.5 mgL⁻¹. The limit of detection for the UV-vis is approximately 0.5 mgL⁻¹ and a limitation of the instrument is it only detects silver particles and does not measure total silver. All column experiments were performed in duplicate and average concentration values are reported.

A plot showing normalized effluent concentration (the concentration at the column outlet divided by the influent concentration) versus dimensionless time (pore volume, PV) was developed for each experiment. This dimensionless breakthrough curve (BTC) of effluent concentration vs time allows for easy comparison between experiments.

Zeroth and first moments of the dimensionless breakthrough curves were calculated. The zeroth moment, which is the area under the breakthrough curve,

represents the total mass of tracer or AgNPs that passed through the column and was in the effluent. Comparing the zeroth moment of the AgNP BTC with the zeroth moment of the nonreactive tracer allows us to quantify the fraction of AgNPs that was retained by the media. Similarly, the first moment represents the mean time tracer and AgNPs were in the column. Comparing the first moment of the AgNP BTC with the first moment of the nonreactive tracer allows us to quantify the retardation of the AgNPs as they are transported through the column.

Analysis

The AgNPs used in these experiments were characterized and reported in Flory et al. (2013). High resolution transmission electron microscopy (HRTEM) was used to measure the shape and size of AgNPs on a Hitachi H-7600 transmission electron microscope at an accelerating voltage of 100 kV. In addition, TEM images were taken on two samples that had passed through the column. X-ray diffraction (XRD) (Bruker D8 Advanced) with a CuK-alpha source was used to identify any metal oxides present on the three sizes of sand.

The contents of the column were retained and analyzed to measure the amount of silver associated with either the water or the amount captured by the sand that was left in the column. After each experiment the contents of the column were placed into sealed plastic tubes. The aqueous solution in the tubes was poured into a sample vial and weighed. 1 mL of nitric acid was added to 9 mL of this solution. EPA method 3015 (USEPA 1997) was then followed to find the concentration of Ag in the solution.

Ten to 15 mL of nitric acid was added to the sand from the tubes, and the samples were centrifuged for 10 minutes at 2000 rpm. The supernatant was poured from the sample and weighed. 1 mL of nitric acid was then added to 9 mL of supernatant. These samples also were analyzed using EPA method 3015 (USEPA 1997) on the ICP.

Finally, to find the amount of AgNPs attached to the sand approximately 1 g of sand was taken from each sample after the supernatant was removed and it was placed on a watch glass and placed in an oven at 105 °C for 12 hours. Then 0.5 g of the dried sand was put into a sample container with 4.5 mL of HNO₃, and 0.5 mL hydrochloric acid. These samples were analyzed with EPA method 3051 (USEPA 1997).

Mass Balance Experiment

An additional experiment was run using coarse sand and a 4 mL min⁻¹ flow rate to evaluate the overall silver mass balance. The column experiment was set up and run as described above; however in the previous experiments once the effluent of the column passed thru the UV-vis for measurement of the AgNPs concentration, it was weighed and then discarded. For this experiment, all 90 effluent samples were retained for further analysis. The odd sample numbers were prepared for inductively coupled argon plasma-optical emission spectroscopy (ICP-OES) analysis. Each of these samples contained approximately 2 mL of solution. From this, 1 mL was taken and 9 mL of DI water was added. Then 1 mL of HNO₃ was added to 9 mL of the diluted solution. The samples were then microwave digested using EPA method 3015 (USEPA 1997) and analyzed on the ICP-OES. This method would account for both dissolved and particulate silver, in contrast to the UV-vis measurement, which would only account for particulate silver.

Influent samples, nominally at a concentration $C_0 = 15 \text{ mg L}^{-1}$, were also analyzed using the ICP. After the experiment was run, 9 mL of the remaining influent solution was taken and 1 mL of HNO_3 was added. After microwave digestion, 1 mL was removed and added to 9 mL of RO water to achieve a dilution factor of 10. The sample was then run on the ICP-OES, to quantify C_0 .

The sand in this mass balance experiment was analyzed as in the previous experiments with one addition. For this experiment, the sand was centrifuged an additional time with 15 mL of nitric acid for 10 minutes at 2000rpm. Again, the supernatant was poured from the sample and weighed. 1 mL of nitric acid was then added to 9 mL of supernatant. This was accomplished to ensure all the captured silver in the sand would be released to be quantified.

Modeling

To help us better describe and understand AgNP transport in porous media, a model was developed. The model incorporates the processes of advection, dispersion, and capture to describe transport in a porous medium. AgNP capture was modeled as both reversible (2nd term on the left-hand side of equation 1) and irreversible (third term on the right-hand side of Equation 1)

$$\theta \frac{\partial N}{\partial t} + \rho \frac{\partial N_s}{\partial t} = D \theta \frac{\partial^2 N}{\partial x^2} - v \theta \frac{\partial N}{\partial x} - \lambda \theta N \quad \text{Eq. 1}$$

Reversible capture was modeled as either a fast equilibrium process (Equation 2) or a rate-limited process (Equation 3).

$$N_s = \frac{k_f}{\alpha} N \quad \text{Eq. 2}$$

$$\frac{\partial N_s}{\partial t} = \alpha \left(\frac{k_f}{\alpha} N - N_s \right) \quad \text{Eq. 3}$$

where N and N_s are the concentrations of suspended and captured nanoparticles, respectively, ρ is the bulk density of the porous medium, θ is the porosity of the porous medium, D is a dispersion coefficient, v is the average pore velocity of the water, t is time, x is length, λ is a first-order irreversible capture rate constant, and k_f and α are first-order capture/release rate constants, respectively. For a clean one-dimensional column with a finite-pulse third type boundary condition at the inlet, the initial and boundary conditions are:

$$N(x, t = 0) = N_s(x, t = 0) = 0 \quad \text{Eq. 4a}$$

$$\begin{aligned} (vN - D \frac{\partial N}{\partial x}) \Big|_{x=0} &= vN_0 & 0 < t < t_p \\ &= 0 & t > t_p \end{aligned} \quad \text{Eq. 4b}$$

$$N(x \rightarrow \infty, t) = 0 \quad \text{Eq. 4c}$$

where nanoparticles at a suspended concentration of N_0 are injected into the column inlet ($x = 0$) for a time period t_p .

A nondimensional version of Equations 1 and 2 is

$$R \frac{\partial \bar{N}}{\partial T} = \frac{1}{Pe} \frac{\partial^2 \bar{N}}{\partial \bar{x}^2} - \frac{\partial \bar{N}}{\partial \bar{x}} - Da_{irrev}^I \bar{N} \quad \text{Eq. 5}$$

where

$T = \frac{vt}{L}$ is a dimensionless time scale, also referred to as pore volume (PV)

$\bar{x} = \frac{x}{L}$ is a dimensionless length scale

L is the length of the column

$\bar{N} = \frac{N}{N_0}$ is a nondimensional suspended nanoparticle concentration

$R = 1 + \frac{\rho \frac{k_f}{\alpha}}{\theta}$ is a retardation factor

$Pe = \frac{vL}{D}$ is a Peclet number, the ratio of a dispersion time scale to an advection

time scale

$Da_{irrev}^I = \frac{\lambda L}{v}$ is a Damkohler number, the ratio of an advection time scale to an

irreversible capture time scale

Nondimensional versions of Equations 1 and 3 are

$$\frac{\partial \bar{N}}{\partial T} + \frac{\partial \bar{N}_s}{\partial T} = \frac{1}{Pe} \frac{\partial^2 \bar{N}}{\partial \bar{x}^2} - \frac{\partial \bar{N}}{\partial \bar{x}} - Da_{irrev}^I \bar{N} \quad \text{Eq. 6}$$

$$\frac{\partial \bar{N}_s}{\partial T} = Da_{rev}^I (\bar{N} - \bar{N}_s) \quad \text{Eq. 7}$$

where

$Da_{rev}^I = \frac{\alpha L}{v}$ is also a Damkohler number, in this case the ratio of an advection

time scale to a reversible capture/release time scale

$\bar{N}_s = \frac{N_s}{\frac{k_f}{\alpha} N_0}$ is a nondimensional attached nanoparticle concentration

The nondimensionalized initial and boundary conditions (corresponding to Equation 4) are:

$$\bar{N}(\bar{x}, T = 0) = \bar{N}_s(\bar{x}, T = 0) = 0 \quad \text{Eq. 8a}$$

$$\begin{aligned} \left(\bar{N} - \frac{1}{Pe} \frac{\partial \bar{N}}{\partial \bar{x}} \right) \Big|_{\bar{x}=0} &= 1 & 0 < T < T_p \\ &= 0 & T > T_p \end{aligned} \quad \text{Eq. 8b}$$

$$\bar{N}(\bar{x} \rightarrow \infty, T) = 0 \quad \text{Eq. 8c}$$

where $T_p = \frac{vt_p}{L}$ is the dimensionless input pulse time

For all the UV-Vis results, we use an analytical solution to Equations 5 and 8 to plot \bar{N} vs T . Pe , R , Da_{irrev}^I , and T_p are used as fitting parameters.

For the ICP results, we use an analytical solution to Equations 6, 7, and 8 (Valocchi and Werth, 2004) to plot \bar{N} vs T . Pe , Da_{rev}^I , Da_{irrev}^I , and T_p are used as fitting parameters.

Results and Discussion

Characterization of AgNPs

The HRTEM image and analysis (Figures 1a and 1b) show results similar to those presented by Flory et al (2013). At the neutral pH used in this study, the diameters of all particles ranged from 4 to 38 nm with 95% of the particles under 25 nm, 4% between 25-30 nm and less than 1% over 31 nm. The average diameter was 16.9 nm.

Characterization of Sand

XRD showed that all sands used were similar to quartz. No metal oxides were found in the crystalline form attached to any of the sand size fractions. Amorphous phase oxides could be present.

X-ray photoelectron spectroscopy (XPS) was performed on the AgNPs to confirm the chemical composition of the nanoparticles' surface. It is found that the top three nanometers of the surface were composed of 75% carbon, 13% oxygen, 10% nitrogen and 1% metallic Ag. The presence of carbon is a result of the coating applied to the AgNP by the manufacturer.

Transport of AgNPs

The dimensionless breakthrough curves for the chloride tracer (Figure 2a) through the coarse sand column at 1 and 4 mL min⁻¹ are shown. Shown in Figure 2b and 2c are the AgNP's BTCs at the 1 and 4 mL min⁻¹ flow rate through the coarse sand. Figure 3a plots the BTCs for the chloride tracer through the medium sand column at 1 and 4 mL min⁻¹. Figures 3b and 3c show the BTCs for AgNPs through the medium sand column at 1 and 4 mL min⁻¹. Table 1 shows the zeroth and first moment for the BTCs. No breakthrough of AgNPs was observed for the fine sand at either flow rate. As a result, no zeroth or first moment is shown for the fine sand.

In Table 2 the ratio of the zeroth and first moments of the AgNP BTCs to the moment of the corresponding tracer BTC is presented. The zeroth moment ratio shows the extent of capture of the AgNPs compared to the tracer, which is assumed to not be captured at all. The first moment ratio shows the extent of retardation compared to the

tracer, which is also assumed to not be retarded at all. Comparing the ratio of the moments at the two flow rates, it can be seen that at least for the fourfold increase in flow studied here, the flow rate had little effect on the transport of AgNPs. In addition, the retardation did not change significantly with the different flow rates in the different types of sand. The retardation observed here differed from what Flory et al. (2013) observed. Flory et al. (2013) found no AgNP retardation in their glass bead media whereas some retardation of the AgNPs was observed in the current study with different types of sand.

When comparing the effects of media size, the medium sand (0.21-0.297 mm) had less retention of AgNPs than the coarse sand (0.4-2 mm) in these experiments as shown by the zeroth moment ratios in Table 2 as well as the data in Figure 4. This is not in accordance with conventional filtration theory which states that with smaller grain size the fraction of mass retained in the media should increase. This also disagrees with Li et al. (2008) who found that retention was increased as the particle size of the media decreased. We speculate that our observation may be attributed to the difference in the size range of the medium vs coarse sand, as opposed to the median grain size difference. The coarse sand had a size range from 0.4-2 mm, and the medium sand had a much narrower range of 0.21-0.291 mm. Zhang et al. (2012) showed similar results in their transport studies with Fullerene nanoparticles in Lula soil. They found that significantly more mass was retained in Lula soil versus Ottawa sand (mainly pure quartz). They attribute this to the irregular and rougher shape and greater heterogeneity of Lula sand compared with Ottawa sand.

Ren and Smith (2013) concluded the size of the media had an effect on the transport of AgNPs. They found increased retention with smaller media diameters. In their study their coarse and medium sand median grain diameters (0.55 and 0.34 mm) were both within the range of our coarse sand (0.2-4 mm). The fine sand used in our experiment had a diameter of < 0.074 mm. The result obtained from our fine sand experiments agree with filtration theory as well as with Li et al. (2008) and Ren and Smith (2013).

As in the other experiments, a BTC was developed for the single mass balance experiment. We found that 17% of the initial mass passed through the column. We also found 71.5% of the silver was captured by the sand. A total of 88.75% of the mass was accounted for in this experiment.

UV-vis measurements were taken along with the ICP-OES measurements (Figure 5). It is clear that more mass is measured in the effluent with the ICP-OES. The difference in mass can be attributed to the UV-vis only measuring AgNPs rather than the total silver as the ICP-OES does. It appears that much of the mass being detected is in the dissolved form. Also the ICP-OES data were able to show that tailing occurred as the experiment continued. This tailing effect can be attributed to the captured silver being dissolved and then measured by the ICP. This dissolved silver tail is not detected by the UV-vis, which only detects particulates.

It was noted that over the several-month course of these experiments, AgNP breakthrough curves could not be replicated, even though experimental conditions were ostensibly the same. Experiments were run five months after the initial experiments in an

attempt to reproduce results previously obtained. It can be seen for the coarse sand at 4 mL min⁻¹ flow rate column experiments run five months apart, there was much less breakthrough of AgNPs measured by the UV-vis after five months (Figure 6). The samples taken at the later experiment were also analyzed by ICP-OES with approximately 89% of the mass accounted for. The influent concentration measured by UV-vis for this experiment was similar to all other experiments run (~15 mgL⁻¹); however it is clear that the effluent concentrations are not similar. One hypothesis is that the PVP coating for the AgNPs has deteriorated after five months and made the particles easier to dissolve into solution. Another hypothesis could be that the PVP deteriorated, causing the NPs to agglomerate and be captured by the media. Then, the captured particles dissolved, resulting in the long tail observed in the ICP. These hypotheses could not be tested at this time.

Model Simulations of AgNP Transport

As can be seen in Figures 2-4, the equilibrium model does a good job in simulating the experimental data. We also see, by comparing Tables 2 and 3, that, as should be expected, the Damkohler number, which indicates irreversible capture, is larger when the 0th moment ratio is smaller, and the retardation factor is larger when the first moment ratio is larger.

From Figure 7, we see that to simulate the transport of total silver, it is necessary to apply a model that assumes both irreversible capture and rate-limited reversible capture. Figure 7 plots the BTC for the coarse 4 mL min⁻¹ flow rate and coarse sand with

data obtained from the ICP-OES analysis. This graph shows that there is tailing of the silver in the experiments. This tailing was not observed in the other experiments, which used the UV-vis to measure silver, because the limits of detection for the UV-vis were higher than those of the ICP and also the UV-vis only detects particles whereas the ICP measures total silver.

Significance

The effect of flow rate and media size on the transport of AgNPs under saturated conditions was examined in this study. It was found through experimentation and mathematical modeling that the flow rate plays a minor role in transport compared to the size of the media. More specifically, the size uniformity of the media appears to play the larger role in affecting transport.

We found that while a medium can have larger average diameters of particles, it can retard and capture more AgNPs than a finer sand that is better sorted. This is relevant in the natural environment because of the differences in media that may be present at different locations. We also confirmed previous studies that AgNPs are filtered out by fine media (<0.074 mm).

Acknowledgements

The support of the Air Force Medical Support Agency's Research and Innovation Division (AFMSA/SG51), Department of Defense Funding Document No. F1ATD42054G001, is gratefully acknowledged. The author would like to thank Ms Jill Webster, Ms Deborah Roose and Christopher A. Impellitteri from the EPA's National

Risk Management Laboratory for their help with ICP analyses and manuscript review, and Ms Barbara Miller from the University of Dayton for the TEM and XRD support.

Disclaimer

The views expressed in this paper are those of the authors and do not reflect the official policy or position of the United States Air Force, The Department of Defense, or the United States Government.

Bibliography

The references of this article are combined with the thesis.

III. Conclusion

Summary of Findings

The effect of flow rate and media size on the transport of AgNPs under saturated conditions was examined in this study. It was found through experimentation and mathematical modeling that the flow rate plays a minor role in transport compared to the size of the media. More specifically, the size uniformity of the media appears to play the larger role in affecting transport.

We found that while a medium can have larger average diameters of particles, it can retard and capture more AgNPs than a finer sand that is better sorted. This is relevant in the natural environment because of the differences in media that may be present at different locations. We also confirmed previous studies that AgNPs are filtered out by fine media (<0.074 mm).

Recommendations for Future Research

Due to the numerous physical, chemical, and even biological factors that may affect transport of ENPs in the environment, along with the rapidly expanding uses of these materials, it is important that we gain a better understanding of how these factors affect ENP fate and transport. While not conclusive, observations in this study point to media heterogeneity as an important factor which affects transport of AgNPs. To test this hypothesis, an experiment could be conducted whereby the coarse sand used in this study is sorted into a more homogenous sand, and AgNP transport in this more homogeneous media compared to transport in the unsorted heterogeneous media. Key to understanding would be quantifying the relative heterogeneities of the different media, perhaps through

use of a uniformity coefficient. Various tests could then be run, comparing transport of ENPs through media with the same median diameters, but with different coefficients of uniformity.

It was noted that the AgNP breakthrough behavior toward the end of the study was significantly different than the behavior observed months earlier, at the study's start, even though conditions (media size, flow rate) were identical. It was hypothesized that over the months the AgNP's PVP coating had changed in some manner as to affect their transport. Experiments to determine if and how the AgNP characteristics change over time, and how these changes affect breakthrough behavior, would be very useful in helping us to understand how these ENPs are transported in the environment.

Table 1: Breakthrough curve moments for AgNP at different flow rates and sand sizes

	0 th moment	1 st moment
Coarse 4 mL min ⁻¹ tracer	4.64	4.07
Coarse 4 mL min ⁻¹	2.14	4.83
Coarse 1 mL min ⁻¹ tracer	4.11	4.25
Coarse 1 mL min ⁻¹	1.69	5.11
Med 4 mL min ⁻¹ tracer	4.75	4.84
Med 4 mL min ⁻¹	2.79	5.25
Med 1 mL min ⁻¹ tracer	5.41	4.75
Med 1 mL min ⁻¹	3.28	4.84

Table 2: Ratio of AgNP to tracer breakthrough curve moments at different flow rates and sand sizes

	0 th moment ratio	1 st moment ratio
Coarse 4 mL min ⁻¹	0.46	1.19
Coarse 1 mL min ⁻¹	0.41	1.20
Med 4 mL min ⁻¹	0.58	1.08
Med 1 mL min ⁻¹	0.61	1.02

Table 3: Model parameter values at different flow rates and sand sizes

	R	Pe	Da_{irrev}^I	T_p
Coarse 1 mL min ⁻¹	3.30	5.26	0.97	4.33
Coarse 4 mL min ⁻¹	2.64	6.67	0.77	4.63
Medium 1 mL min ⁻¹	1.15	0.46	0.40	6.9
Medium 4 mL min ⁻¹	2.43	1.92	0.71	6.25

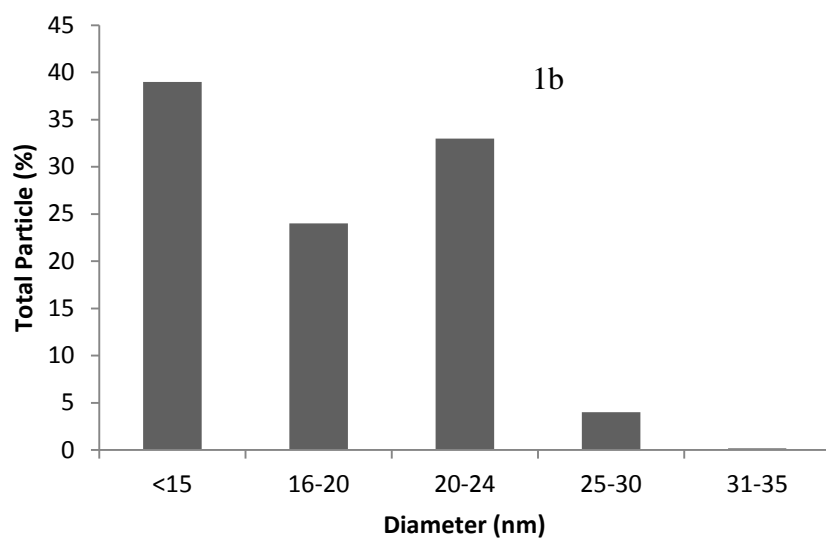
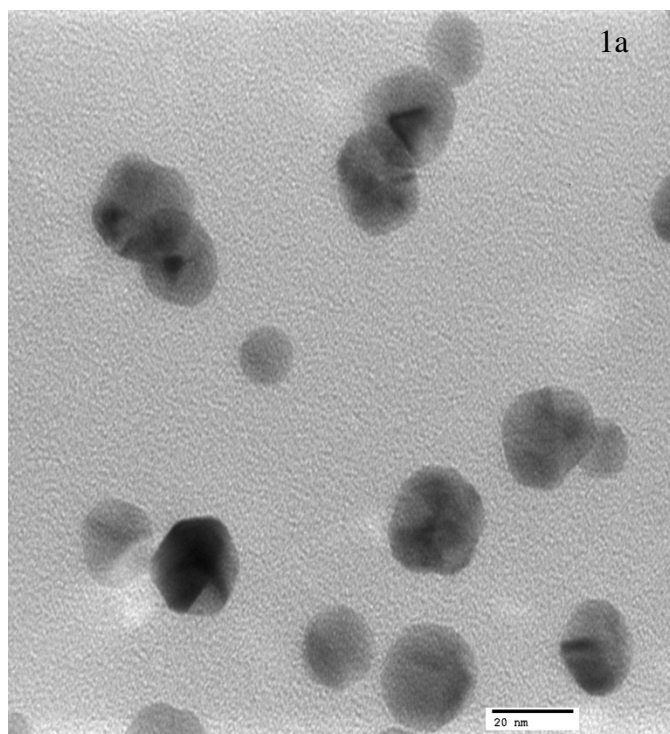


Figure 1: a) HRTEM images of AgNPs and b) size histograms prepared based on analysis of the HRTEM images of > 500 AgNPs.

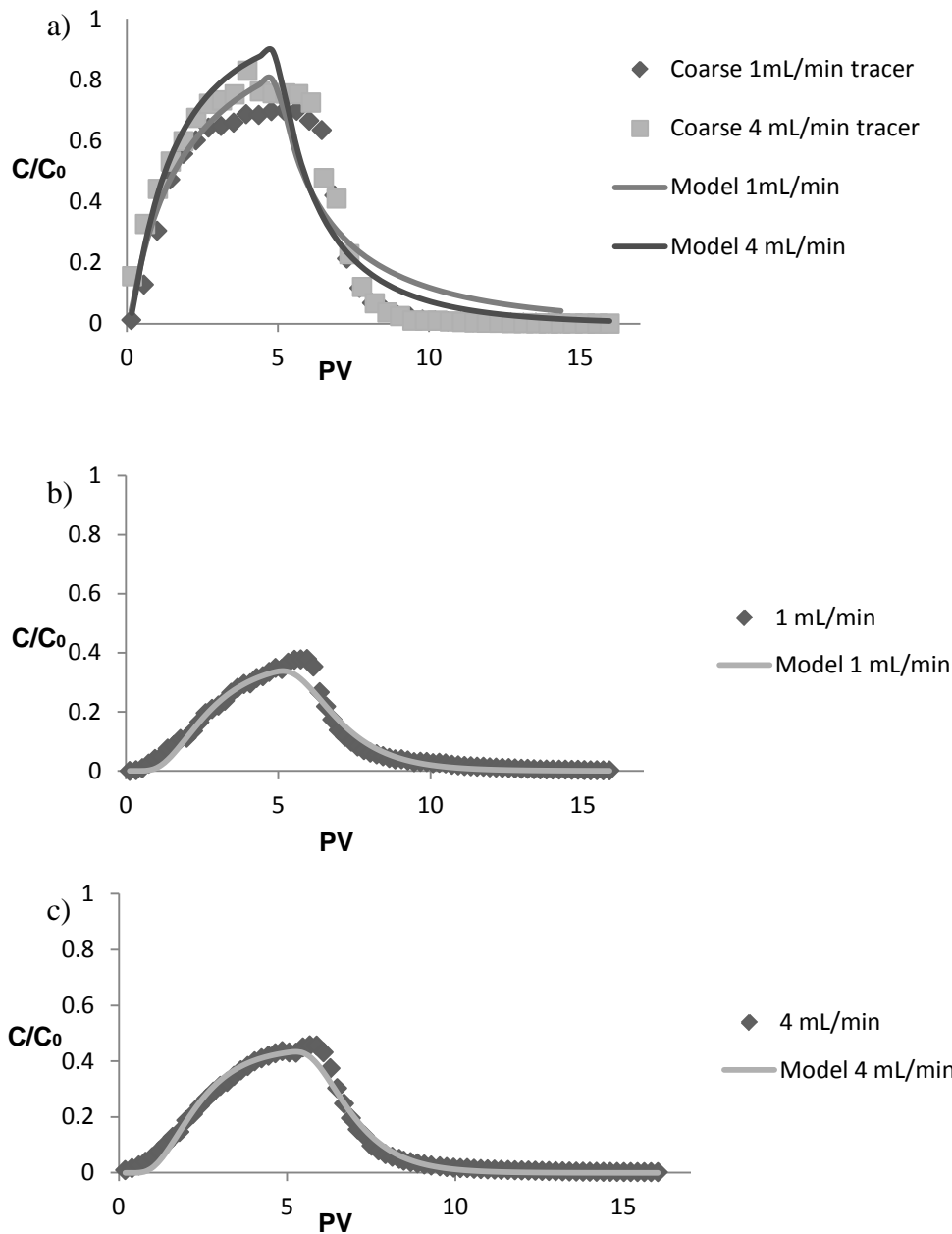


Figure 2: Coarse sand BTC for a) tracer data and model simulation for 1 and 4 mL min⁻¹ flow rates b) AgNP data and model simulation for 1 mL min⁻¹ flow rate c) AgNP data and model simulation for 4 mL min⁻¹ flow rate

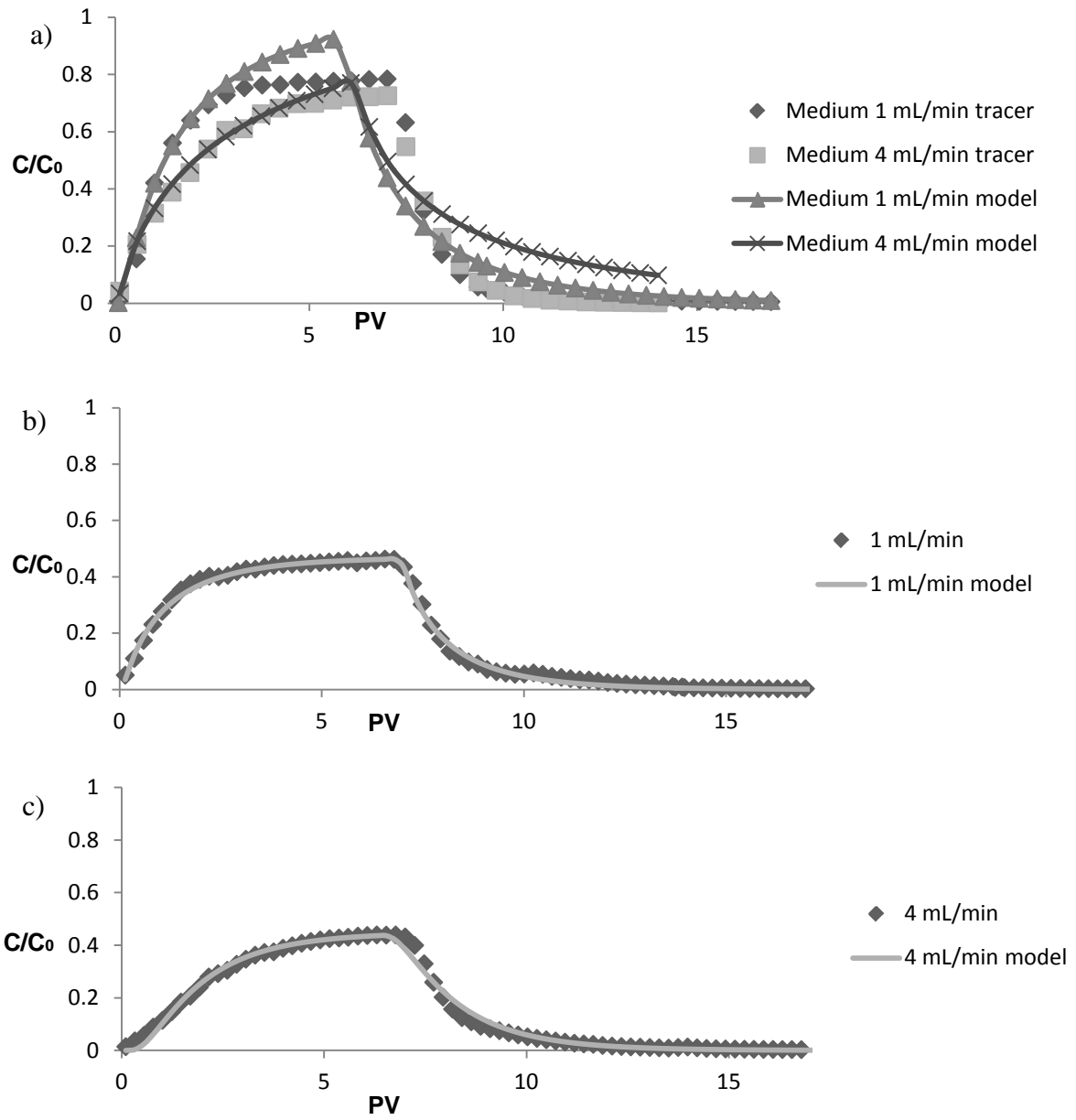


Figure 3: Medium sand BTC for a) tracer data and model simulation for 1 and 4 mL min⁻¹ flow rates b) AgNP data and model simulation for 1 mL min⁻¹ flow rate c) AgNP data and model simulation for 4 mL min⁻¹ flow rate

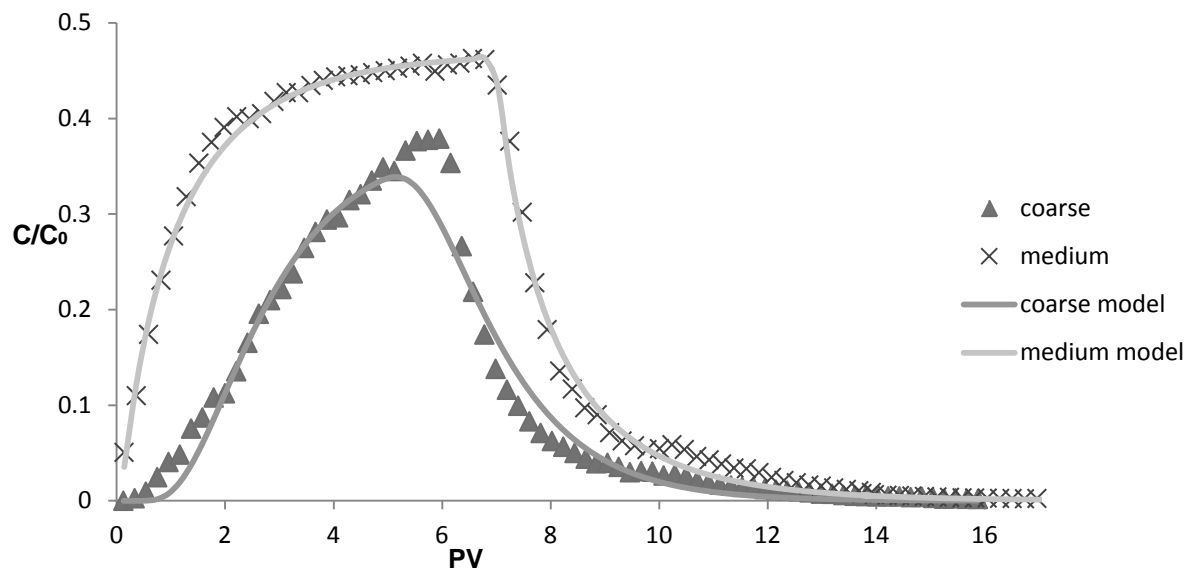


Figure 4: BTC for AgNPs through coarse and medium sand columns and 1 mL min^{-1} flow rates with the corresponding model simulations

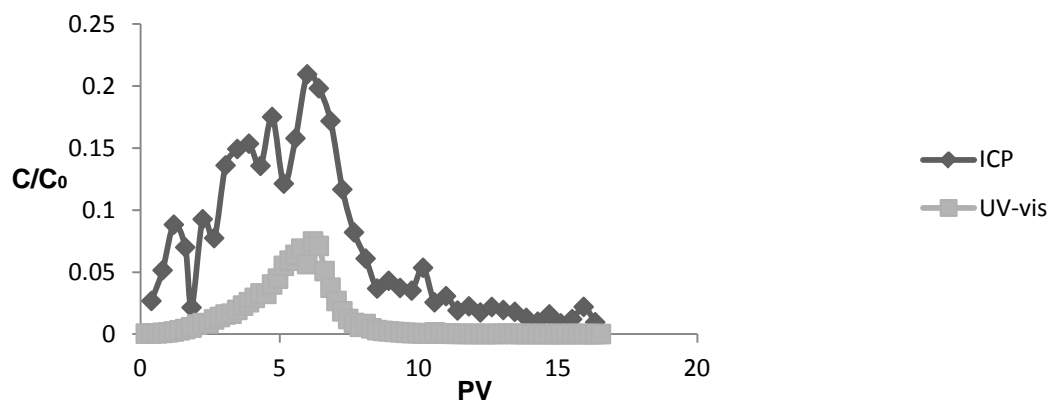


Figure 5: AgNP BTCs for coarse sand column and 4 mL min^{-1} flow rates plotted comparing ICP and UV-vis data

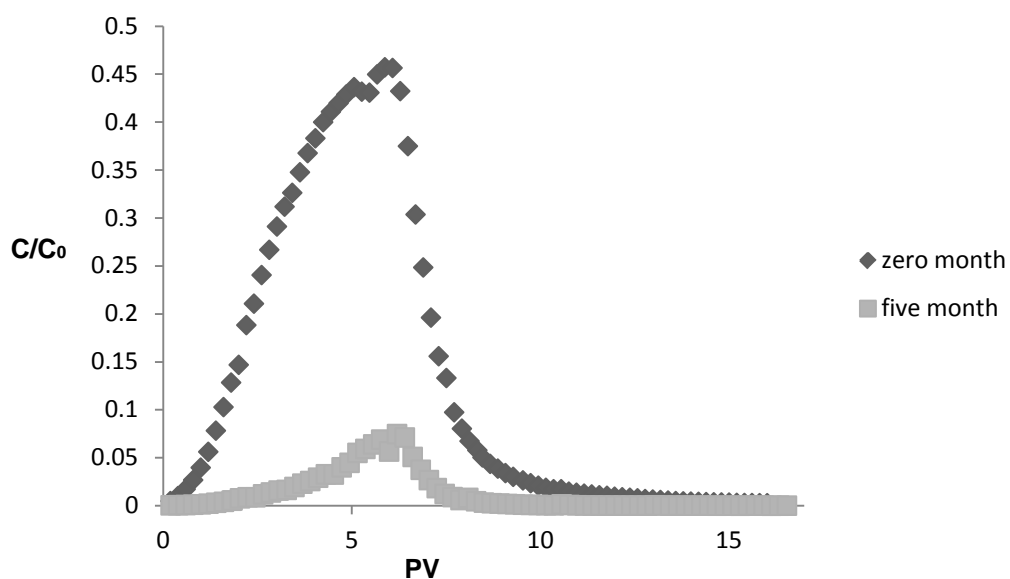


Figure 6: AgNP BTCs for the coarse sand column and a 4 mL min^{-1} flow rate taken at time zero and after five months measured with UV-Vis

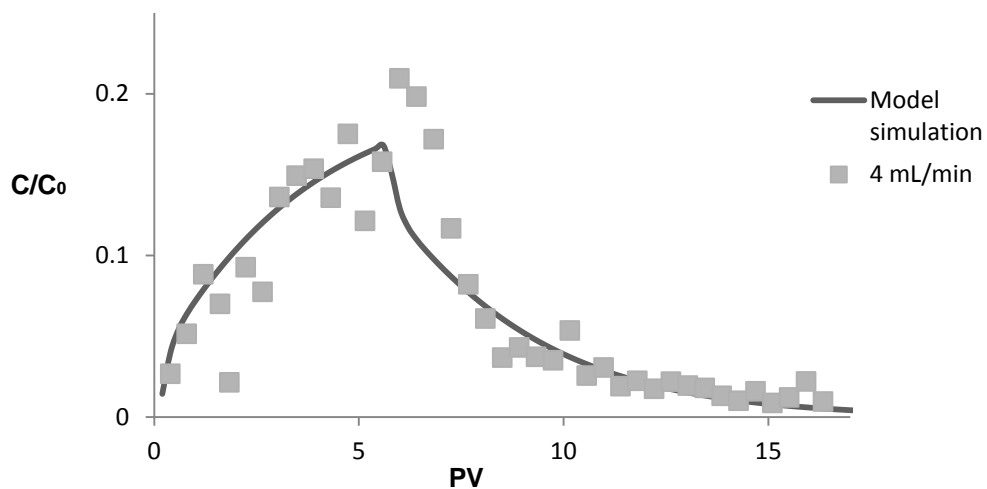


Figure 7: AgNP BTC data measured on the ICP-OES and model simulation for the coarse sand column and a 4 mL min^{-1} flow rate

Bibliography

- Benn, T., Cavanagh, B., Hristovski, K., Posner, J.D., Westerhoff, P. (2010). "The Release of Nanosilver from Consumer Products Used in the Home." *Journal of Environmental Quality*, 39 (6):1875-1882.
- Chowdhury, I., Hong, Y., Honda, R. J., & Walker, S. L. (2011). "Mechanisms of TiO₂ nanoparticle transport in porous media: Role of solution chemistry, nanoparticle concentration, and flowrate." *Journal of Colloid and Interface Science*, 360(2): 548-555.
- Faunce, T., Watal, A. (2010). "Nanosilver and global public health: international regulatory issues." *Nanomedicine*, 5 (4):617-632.
- Flory, J., Kanel, S., Racz, L., Impellitteri, C., Silva, R., & Goltz, M. (2013). "Influence of pH on the transport of silver nanoparticles in saturated porous media: laboratory experiments and modeling." *Journal of Nanoparticle Research*, 15:1484.
- Godinez, I. G., & Darnault, C. J. (2011). "Aggregation and transport of nano- TiO₂ in saturated porous media: Effects of pH, surfactants and flow velocity." *Water Research*, 45(2): 839-851.
- Impellitteri, C., A., Tolaymat, T., M., Scheckel, K.,G. (2009). "The Speciation of Silver Nanoparticles in Antimicrobial Fabric Before and After Exposure to a Hypochlorite/Detergent Solution." *Journal of Environmental Quality*, 38 (4):1528-1530.
- Kennedy, A. J., Hull, M. S., Bednar, A. J., Goss, J. D., Gunter, J. C., Bouldin, J. L., Vikesland, P. J., Steevens, J. A., and Kennedy, A. J. (2010). "Fractionating Nanosilver: Importance for Determining Toxicity to Aquatic Test Organisms." *Environmental Science & Technology*, 44(24): 9571-9577.
- Kim, Y. S., Kim, J. S., Cho, H. S., Rha, D. S., Kim, J. M., Park, J. D., Choi, B. S., Lim, R., Chang, H. K., Chung, Y. H., Kwon, I. H., Jeong, J., Han, B. S., and Yu, I. J. (2008). "Twenty-Eight-Day Oral Toxicity, Genotoxicity, and Gender-Related Tissue Distribution of Silver Nanoparticles in Sprague-Dawley Rats." *Inhalation Toxicology*, 20(6): 575-583.
- Kim, J.S., Kuk, E., Yu, K.N., Kim, J.H., Park, S.J., Lee, H.J., Kim, S.H., Park, Y.K., Park, Y.H., Hwang, C.Y., Kim, Y.K., Lee, Y.S., Jeong, D.H., Cho, M.H. (2007). "Antimicrobial effects of silver nanoparticles." *Nanomedicine-Nanotechnology Biology and Medicine*, 3 (1): 95-101.

- Lecoanet, H. F., & Wiesner, M. R. (2004). "Velocity effects on fullerene and oxide nanoparticle deposition in porous media." *Environmental Science & Technology*, 38(16): 4377-4382.
- Li, Y., Wang, Y., Pennell, K. D., & Abriola, L. M. (2008). "Investigation of the transport and deposition of fullerene (C60) nanoparticles in quartz sands under varying flow conditions." *Environmental Science & Technology*, 42(19): 7174-7180.
- Mattison, N. T., O'Carroll, D. M., Kerry Rowe, R., & Petersen, E. J. (2011). "Impact of porous media grain size on the transport of multi-walled carbon nanotubes." *Environmental Science & Technology*, 45(22): 9765-9775.
- Mossa Hosseini, S., & Tosco, T. (2013). "Transport and retention of high concentrated nano-Fe/Cu particles through highly flow-rated packed sand column." *Water Research*, 47(1): 326-338.
- Park, Y., Atwill, E. R., Hou, L., Packman, A. I., & Harter, T. (2012). "Deposition of *Cryptosporidium parvum* Oocysts in Porous Media: A Synthesis of Attachment Efficiencies Measured under Varying Environmental Conditions." *Environmental Science & Technology*. 46(17): 9491-9500.
- Petosa, A. R., Brennan, S. J., Rajput, F., & Tufenkji, N. (2011). "Transport of two metal oxide nanoparticles in saturated granular porous media: Role of water chemistry and particle coating." *Water Research*, 46(4): 1273-1285.
- Quevedo, I. R., & Tufenkji, N. (2012). "Mobility of Functionalized Quantum Dots and a Model Polystyrene Nanoparticle in Saturated Quartz Sand and Loamy Sand." *Environmental Science & Technology*, 46(8): 4449-4457.
- Raychoudhury, T., Naja, G., & Ghoshal, S., (2010). "Assessment of transport of two polyelectrolyte-stabilized zero-valent iron nanoparticles in porous media." *Journal of Contaminant Hydrology*, 118(3): 143-151.
- Redman, J. A., Grant, S. B., Olson, T. M., & Estes, M. K. (2001). "Pathogen filtration, heterogeneity, and the potable reuse of wastewater." *Environmental Science & Technology*, 35(9): 1798-1805.
- Ren, D., & Smith, J. A. (2013). "Protein-Capped Silver Nanoparticle Transport in Water-Saturated Sand." Accepted *Journal of Environmental Engineering*, DOI: 10.1061/(ASCE)EE.1943-7870.0000684.
- Sagee, O., Dror, I., & Berkowitz, B., (2012). "Transport of silver nanoparticles (AgNPs) in soil." *Chemosphere*, 88(5): 670-675.

- Schrand, A. M., Rahman, M. F., Hussain, S. M., Schlager, J. J., Smith, D. A., and Syed, A. F., (2010). "Metal-Based Nanoparticles and Their Toxicity Assessment." *WIREs Nanomedicine and Nanobiotechnology*, 2: 544-568.
- Shaw, B. J., and Handy, R. D., (2011). "Physiological Effects of Nanoparticles on Fish: A Comparison of Nanometals Versus Metal Ions." *Environment International*, 37(6): 1083-1097.
- Silliman, S. E., Dunlap, R., Fletcher, M., & Schneegurt, M. A. (2001). "Bacterial transport in heterogeneous porous media: Observations from laboratory experiments." *Water Resources Research*, 37(11): 2699-2707.
- Tolaymat TM, El Badawy AM, Genaidy A, Scheckel KG, Luxton TP, Suidan M (2010). "An evidencebased environmental perspective of manufactured silver nanoparticle in syntheses and applications: A systematic review and critical appraisal of peer-reviewed scientific papers." *Sci Total Environ*, 408(5): 999-1006.
- Tosco, T., Bosch, J., Meckenstock, R. U., & Sethi, R. (2012). "Transport of ferrihydrite nanoparticles in saturated porous media: role of ionic strength and flow rate." *Environmental Science & Technology*, 46(7): 4008-4015.
- USEPA (1997) Method 3015A: Microwave assisted acid digestion of aqueous samples and extracts. 2nd ed. in SW846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods.
- USEPA (1997) Method 3051A: Microwave assisted acid digestion of sediments, sludges, soils, and oils. 2nd ed. in SW846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods.
- Valocchi, A.J. and C.J. Werth, Web-based interactive simulation of groundwater pollutant fate and transport, *Computer Appl. in Engr. Educ.*, 12(2):75-83, 2004.
- Wang, C., Bobba, A. D., Attinti, R., Shen, C., Lazouskaya, V., Wang, L. P., & Jin, Y. (2012). "Retention and Transport of Silica Nanoparticles in Saturated Porous Media: Effect of Concentration and Particle Size." *Environmental Science & Technology*, 46(13): 7151-7158.
- Wijnhoven, S. W. P., Peijnenburg, W., Herberts, C. A., Hagens, W. I., Oomen, A. G., Heugens, E. H. W., Roszek, B., Bisschops, J., Gosens, I., Van de Meent, D., Dekkers, S., De Jong, W. H., Van Zijverden, M., Sips, A., and Geertsma, R. E. (2009). "Nano-Silver: A Review of Available Data and Knowledge Gaps in Human and Environmental Risk Assessment." *Nanotoxicology*, 3(2): 109-138.

Yao, K. M., Habibian, M. T., & O'Melia, C. R. (1971). "Water and waste water filtration. Concepts and applications." *Environmental Science & Technology*, 5(11): 1105-1112.

Zhang, L., Hou, L., Wang, L., Kan, A. T., Chen, W., & Tomson, M. B. (2012). "Transport of Fullerene Nanoparticles (n C60) in Saturated Sand and Sandy Soil: Controlling Factors and Modeling." *Environmental Science & Technology*, 46(13): 7230-7238.

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 074-0188	
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of the collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 21 Mar 2013		2. REPORT TYPE Master's Thesis		3. DATES COVERED (From - To) Oct 11 -Mar 13	
4. TITLE AND SUBTITLE Influence of Media Size and Flow Rate on the Transport of Silver Nanoparticles in Saturated Porous Media: Laboratory Experiments and Modeling				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Meidinger, Travis J., Major, USAF				5d. PROJECT NUMBER FIATD42054G001	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(S) Air Force Institute of Technology Graduate School of Engineering and Management (AFIT/EN) 2950 Hobson Way WPAFB OH 45433-7765				8. PERFORMING ORGANIZATION REPORT NUMBER AFIT-ENV-13-M-15	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AF Clinical Investigations Program, Office of the Air Force Surgeon General Directorate for Modernization Nereyda Sevilla, MPH, CAsP, PMP, CIV, HSO/Aerospace Physiologist 5201 Leesburg Pike, Suite 1501, Falls Church, VA 22041 Phone: 703-681-6383 (DSN: 761), Nereyda.sevilla@pentagon.af.mil				10. SPONSOR/MONITOR'S ACRONYM(S) AFMSA/SGSI	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT DISTRIBUTION STATEMENT A: APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED					
13. SUPPLEMENTARY NOTES This material is declared a work of the U.S. Government and is not subject to copyright protection in the United States.					
14. ABSTRACT Silver nanoparticles (AgNPs) are widely produced and used. Because of their potential toxicity and the possibility of their release into the environment, it is important to understand the factors involved in their transport; particularly how they may move in groundwater, which is a potential pathway to human and environmental receptors. By passing a solution of 15 mg/L AgNPs with an average size of 17 nm through sand-filled glass columns, this study looks at the physical effects of flow rate and media size on transport. Three different sand sizes (< 0.074, 0.21-0.297, and 0.4-2.0mm) were used, as well as two different flow rates (1 and 4 mL min ⁻¹). Results showed that flow rate had little effect on the transport of AgNPs. As had been found in previous studies, transport through fine sand (< 0.074 mm) was inhibited, and no AgNPs were observed in the column effluent. In contrast to other studies and conventional filtration theory, however, it was observed that more AgNPs were captured in the coarse sand (0.4-2.0 mm) than the medium sand (0.21-0.297 mm). This deviation from conventional filtration theory was attributed to the more heterogeneous size distribution of the coarse sand compared to the medium sand.					
15. SUBJECT TERMS Silver nanoparticles, nanomaterials, fate and transport, advection-dispersion model					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 45	19a. NAME OF RESPONSIBLE PERSON LEEANN RACZ, Maj, USAF, BSC, PhD, PE
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U			19b. TELEPHONE NUMBER (Include area code) (937) 255-3636, x 4711 (leeann.racz@afit.edu)

Standard Form 298 (Rev. 8-98)